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3,565,804

LUBRICATING OIL ADDITIVES

Lewis R. Honnen, Petaluma, Calif., and Robert Gordon Anderson, Wassenaar, Netherlands, assignors to Chevron Research Company, San Francisco, Calif., a corporation of Delaware

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U.S. Cl. 252—50 23 Claims

ABSTRACT OF THE DISCLOSURE

Hydrocarbon polyamines are provided having a long, substantially aliphatic, oil solubilizing hydrocarbon chain bonded to a di- or higher polyamine which find use as detergents and dispersants in both lubricating oils and in fuels. The hydrocarbon group is normally branched and derived from natural sources or polyolefins.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 488,775, filed Sept. 20, 1965, and Ser. No. 408,686, filed Nov. 3, 1964.

BACKGROUND OF THE INVENTION

Field of the invention

The compounds of this invention are long chain hydrocarbon substituted polyamines, the amino groups being bonded to aliphatic carbon atoms. The hydrocarbon group is an oil solubilizing group relatively free of aromatic unsaturation.

These compounds are effective detergents and dispersants in both lubricating oils and fuels for internal combustion engines. In internal combustion engines, the presence of constricted openings and narrow tolerances in the areas of moving parts provides numerous opportunities for deposits to seriously reduce the operating efficiency of the engines. The lubricating oil must be capable of maintaining sludge forming deposits dispersed in the oil, thus keeping the piston and piston rings relatively free of deposits. Also, sludge formation is minimized in the crankcase and in the areas where valves and gears operate.

In addition, the additives of this invention do not themselves contribute significantly to the formation of sludge and deposits. They are able to stably disperse deposit-forming materials in the oil medium, while avoiding any significant enhancement of the rate of formation of deposit-forming materials by their own degradation products.

Description of the prior art

Patents of interest include the following. U.S. Pat. No. 3,182,024 is concerned with a N-amino alkyl or polyamino polyalkylene long chain hydrocarbon substituted pyrrolidine which finds use as a detergent in lubricating oil.

U.S. Pats. Nos. 3,031,505 and 3,189,652 are concerned with hydrocarbon substituted alkylene polyamines, primarily propane diamines and amine compounds up to C₄₀. These compounds are used as reactants to be reacted with glycidyl halides followed by reaction with alkylene polyamines. The final product finds use in maintaining sediment-forming materials dispersed in fuels. The only exemplification are C₁₈ straight chain aliphatic substituted propane diamines.

U.S. Pats. Nos. 2,267,204, 2,267,205, 2,361,457 and 2,891,850 are all concerned with low molecular weight polyamines.

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SUMMARY OF THE INVENTION

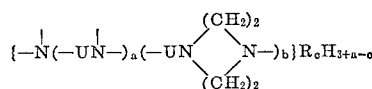
Long branched chain, primarily aliphatic, hydrocarbon substituted polyamines are provided of from about 600 to 10,000 average molecular weight which are effective detergents in lubricating oils and fuels. The hydrocarbon group will normally be derived from mineral oils of high molecular weight or polyolefins by halogenation of the hydrocarbon and displacement of the halogen with an appropriate polyamine, normally free of unsaturation.

DETAILED DESCRIPTION OF THE INVENTION

The compositions of this invention are high molecular weight branched chain aliphatic hydrocarbon N-substituted alkylene polyamines which are superior detergents and dispersants in both lubricating oils and hydrocarbonaceous fuels for internal combustion engines, being effective under wide variations in operating conditions. The compositions have average molecular weights in the range of about 600 to 10,000, more usually in the range of about 750 to 5,000. With the lower molecular weight hydrocarbon groups, the average number of groups will be greater than one. The hydrocarbon groups will normally be aliphatic, having from 0 to 2 sites of unsaturation, more usually from 0 to 2 sites of ethylenic unsaturation and preferably from 0 to 1 site of ethylenic unsaturation.

The hydrocarbon group will normally be derived from a polyolefin derived from olefins of from 2 to 6 carbon atoms (ethylene being copolymerized with an olefin of at least 3 carbon atoms), or from a high molecular weight petroleum-derived hydrocarbon.

For the most part, the compositions of this invention will have the following formula:



wherein:

U is alkylene of from 2 to 6 carbon atoms, more usually of from 2 to 3 carbon atoms, there being at least 2 carbon atoms between the nitrogen atoms;

a is an integer of from 0 to 10, usually of from 1 to 6, and more usually of from 1 to 4;

b is an integer of from 0 to 1 and preferably 0;

a+2b is an integer of from 1 to 10, more usually an integer of from 1 to 6 and preferably an integer of from 1 to 4;

c is an integer or fractional number (when averaged over the entire composition) in the range of from 1 to 5, preferably 1 to 3, and equal to or less than the number of nitrogen atoms in the molecule, usually on the average less than the total number of nitrogen atoms in the molecule; and

R is an aliphatic or alicyclic branched chain hydrocarbon radical derived from petroleum hydrocarbons or olefin monomers of from 2 to 6 carbon atoms, preferably of from 3 to 4 carbon atoms, ethylene being copolymerized with a higher homologue (an olefin of at least 3 carbon atoms) and having from 0 to 2 sites of aliphatic unsaturation, more usually from 0 to 2 sites of ethylenic unsaturation and preferably from 0 to 1 site of ethylenic unsaturation having greater than 40 carbon atoms and not more than 300 carbon atoms, more usually 50 to 200 carbon atoms and preferably 60 to 200 carbon atoms.

The alkylene radical, indicated as U, will have from 2 to 6 carbon atoms, the nitrogens connected by U being separated by at least 2 carbon atoms. The alkylene group may be straight chain or branched chain, the remaining valences of the alkylene group being on different carbon

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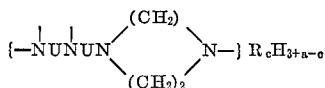
atoms. Illustrative alkylene groups include ethylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, 1,2-propylene, 2-methyl-1,3-propylene, 1,4-(2,3-dimethylbutylene), etc.

The hydrocarbon radical indicated by R may be aliphatic or alicyclic and, except for adventitious amounts of aromatic structure present in petroleum mineral oils, will be free of aromatic unsaturation. The hydrocarbon groups are derived from petroleum mineral oil or polyolefins, either homo-polymers or higher order polymers, of 1-olefins of from 2 to 6 carbon atoms, ethylene being polymerized with a higher homologue. The olefins may be mono- or polyunsaturated, but the polyunsaturated olefins require that the final product be reduced to remove substantially all of the residual unsaturation.

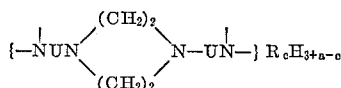
Illustrative sources for the high molecular weight hydrocarbons from petroleum mineral oils are naphthenic bright stocks. For the polyolefin, illustrative polymers include polypropylene, polyisobutylene, poly-1-butene, copolymer of ethylene and isobutylene, copolymer of propylene and isobutylene, poly-1-pentene, poly-4-methyl-1-pentene, poly-1-hexene, poly-3-methylbutene-1, etc.

The hydrocarbon group will normally have at least 1 branch per 6 carbon atoms along the chain, preferably at least 1 branch per 4 carbon atoms along the chain, and particularly preferred that there be from 0.5 to 1 branch per carbon atom along the chain (at least 1 branch per 2 carbon atoms along the chain). These branched chain hydrocarbon groups are readily prepared by the polymerization of olefins of from 3 to 6 carbon atoms and preferably from olefins of from 3 to 4 carbon atoms. The addition polymerizable olefins employed are normally 1-olefins. The branch will be of from 1 to 4 carbon atoms, more usually of from 1 to 2 carbon atoms and preferably methyl.

The above formula provides for alkylene polyamines and alkylene amines and polyamines attached to a piperazine ring. Therefore, when *a* and *b* are both 1 the formulae would be as follows:

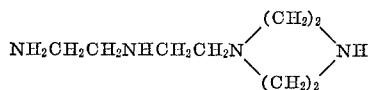


or

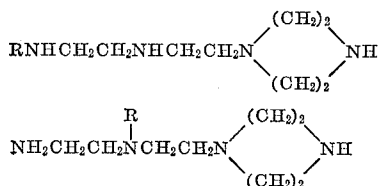


The hydrocarbon group can be bonded to any of the nitrogen atoms which still have an available valence, as indicated by the horizontal and vertical bars. Those valences, not satisfied by an R group, will be satisfied by a hydrogen atom.

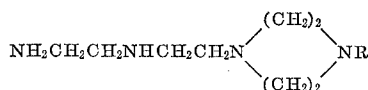
For example, if one combined N-[N'-(2'-aminoethyl-ene)-2-aminoethylene]piperazine, i.e.,



with RX, where the R group will replace from one to two of the hydrogen atoms, a complex product would be obtained. There are three different nitrogen atoms which may react to form a mono-substituted product. The three isomers are:



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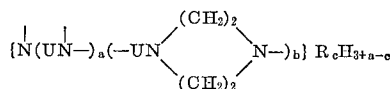


and

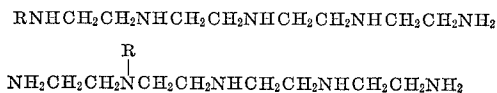
The disubstituted product would add three more compounds.

In order to include all possible variations, the generic formula does not indicate to which nitrogen atom the R group and the H atoms are bonded. Rather, free valences are indicated by bars, and the total number of R groups and H atoms indicated next to the basic polyamine structure. The generic formula employed provides a simple means for including the possible variations that will occur when a polyamine is used having nonequivalent amine nitrogen atoms.

Looking at Example 1, *infra*, where a monopolyisobutenyl tetraethylene pentamine is prepared, for that compound, the generic formula:



would have *a* equal to 4, *b* equal to 0, *c* equal to 1, U would be ethylene, and R would be a polyisobutenyl group of approximately 930 average molecular weight. The three possible mono(polyisobutenyl) tetraethylene pentamines would have the following formulae:



and



It is possible to prepare single compounds. With monopolyisobutenyl ethylene diamine, only one isomer can be formed:



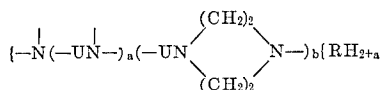
where R is a polyisobutenyl group. With higher order polyamines, while it is possible to form a single isomer, as a practical matter, this will rarely be done.

In preparing the compositions of this invention, rarely will a single compound be employed. With both the polymers and the petroleum-derived hydrocarbon groups, the composition is a mixture of materials having varying structures and molecular weights. Therefore, in referring to molecular weight, viscosity average molecular weights are intended. Furthermore, when speaking of the particular hydrocarbon group, it is intended that the group include the mixture that is normally contained with materials which are commercially available; that is, polyisobutylene is known to have a range of molecular weights and may also include very small amounts of very high molecular weight materials. Furthermore, depending on the method of preparation, the end group of the polymer may vary and may be terminated, not only with an isobutene group, but also with a 1- or 2-butene group.

In addition the alkylene polyamines which are commercially available are frequently mixtures of various alkylene polyamines having one or two species dominating. Thus, in commercially available tetraethylene pentamine, there will also be small amounts of pentaethylene hexamine and triethylene tetramine. In referring to tetraethylene pentamine, for example, it is intended not only to include the pure compound, but those mixtures which are obtained with commercially available alkylene polyamines. Finally, as indicated, in preparing the compounds of this invention, where the various nitrogen atoms of the alkylene polyamine are not equivalent, the product will be a mixture of the various possible isomers.

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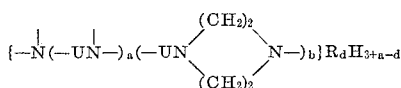
As is evident from the above formula, the alkylene polyamines may have only one hydrocarbon substituent or may be polysubstituted with hydrocarbon radicals. The monosubstituted alkylene polyamine compositions will have the following formula:



wherein U, a, b and R have been previously defined.

Illustrative compounds within the above formula are as follows: N-polyisobutenyl ethylene diamine, N-propenyl ethylene diamine, N - poly(1 - butenyl) ethylene diamine, N-(alternating copolymer of ethylene and isobutylene) ethylene diamine (alternating copolymers of ethylene and isobutylene may be achieved by the cationic polymerization of 4 - methylpentene - 1), N-polypropenyl 2 - aminoethylpiperazine, N - polyisobutenyl 2 - aminoethylpiperazine, N - polypropenyl diethylene triamine, N-polyisobutenyl diethylene triamine, N - poly(1-pent-ayl) diethylene triamine, N - polypropenyl trimethylene diamine, N - polyisobutenyl trimethylene diamine, N - polypropenyl di(trimethylene) triamine, N - polyisobutenyl di(trimethylene) triamine, N-polyisobutenyl 1,2 - propylene diamine, N - polyisobutenyl di(1,2 - propylene) triamine, N - polypropenyl triethylene tetramine, N - polyisobutenyl triethylene tetramine, N - (alternating copolymer of ethylene and isobutylene) triethylene tetramine, N - polypropenyl tetraethylene pentamine, N - polyisobutenyl tetraethylene pentamine, N-polyisobutenyl pentaethylene hexamine, etc.

The polyhydrocarbon radical substituted alkylene polyamine compositions have the following formula:



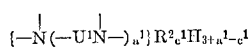
wherein U, a, b and R are as defined previously and d is a fractional or whole number greater than 1 and up to 5, more usually from about 1.2 to 4 and preferably from about 1.5 to 4, averaging over the entire composition.

(As indicated by the above formula, the number of hydrocarbon substituents need not be a whole number when averaging over the total composition; generally, a mixture will be obtained containing mono-, di-, and tri- or higher substituted molecules averaging out to a fractional or whole number.) The hydrocarbon groups may be the same or different, differing both as to molecular weight and structure. Normally, the hydrocarbon groups will be primarily the same structure and differ only as to molecular weight.

It is preferred with the shorter hydrocarbon chains ranging toward the lower end of the molecular weight range to have on the average more than one hydrocarbon group, particularly as the number of amine nitrogens per molecule increases.

Illustrative compounds coming within the above formula are as follows: N,N'-di(polypropenyl) diethylene triamine, N,N' - (polyisobutenyl) diethylene triamine, N,N' - di(polyisobutenyl) triethylene tetramine, N,N' - di(polypropenyl) tetraethylene pentamine, N,N' - di(polyisobutenyl) tetraethylene pentamine, N,N',N'' - tri(polyisobutenyl) tetraethylene pentamine, N,N' - di(polyisobutenyl) 2 - aminoethylpiperazine, N,N' - di(polyisobutenyl) di(trimethylene) triamine, etc.

Usually, the compositions of this invention will have the following formula:



wherein:

U¹ is alkylene of from 2 to 3 carbon atoms (ethylene or propylene) and preferably ethylene;

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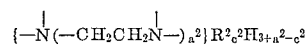
a¹ is an integer of from 1 to 5, more usually of from 1 to 4;

c¹ is an integer of from 1 to 5, more usually of from 1 to 3 and (on the average) equal to or less than the number of nitrogen atoms; and

R¹ is a branched chain aliphatic hydrocarbon group having from 0 to 2 sites of olefinic unsaturation derived from olefins of from 2 to 6 carbon atoms (ethylene is copolymerized with an olefin of at least 3 carbon atoms) and preferably derived from olefins of from 3 to 4 atoms, being either a homopolymer or higher order polymer (co-, ter-, etc.) and having a molecular weight in the range of about 600 to 2800, more usually of from about 750 to about 2000. The preferred R groups are polypropylene, polyisobutylene or combinations thereof.

When c¹ is equal to one, the alkenylene polyamine will be mono-substituted. When c¹ is greater than 1, usually averaging over the entire composition in the range of about 1.25 to 3, the alkylene polyamine will normally be a mixture of mono- and higher order substitution.

Commonly available alkylene polyamines are the ethylene polyamines having from 2 to 6 amino nitrogen groups. When these are substituted with a branch chain aliphatic hydrocarbon group, these compositions will have the following formula:



wherein:

a² is an integer of from 1 to 5, more usually from 1 to 4;

c² is an integer or fractional number of from 1 to 4, more usually of from 1 to 3 and preferably being in the range of about 1 to 2; and

R² is a branched chain aliphatic hydrocarbon group derived from polymerizing olefins of from 3 to 4 carbon atoms and having a molecular weight in the range of about 650 to 2800, more usually 750 to 2000. Preferred R²'s are polypropenyl, polyisobutenyl or combinations thereof, either mixtures or copolymers.

METHOD OF PREPARATION

The compositions of this invention are readily prepared by combining an aliphatic or alicyclic halide with the desired amine in the proper mole proportions. The halide is prepared from the hydrocarbon by halogenation: ionically or free radically.

As already indicated, the hydrocarbon groups may be prepared by ionic or free radical polymerization of olefins of from 2 to 6 carbon atoms (ethylene must be copolymerized with another olefin) to an olefin of the desired molecular weight. The olefins which find use are ethylene, propylene, isobutylene, 1-butene, 1-pentene, 3--methyl-1-pentene, 4 - methyl-1-pentene, etc., preferably propylene and isobutylene.

As previously indicated, there should be at least 1 propylene, isobutylene, 1-butene, 1-pentene, 3-methyl-1-branch per 4 carbons along the chain and preferably at least 1 branch per 4 carbons along the chain. The preferred olefins, propylene and isobutylene, have from 0.5 to 1 branch per atom along the hydrocarbon chain.

Alternatively, various naturally occurring materials may be used which have the desired molecular weight and aliphatic or alicyclic character.

The halogen may be introduced into the hydrocarbon molecule by various means known in the art. Most readily, either chlorine or bromine (halogen of atomic number 17-35) may be introduced by the free radical catalyzed halogenation of the hydrocarbon, or ionic addition to olefinic unsaturation. Various free radical catalysts may be used, such as peroxides, azo compounds, bromine, iodine, as well as light. Ionic catalysts are exemplified by ferric chloride. Methods of halogenation are well known in the art and do not require extensive exemplification or illustration here.

The amount of halogen introduced will depend on the particular hydrocarbon used, the desired amount of amine to be introduced into the molecule, the particular alkylene amine used, and the halogen used. The amount of halogen introduced will generally be in the range from about 1 to 5 halogen atoms per molecule, depending on the reactivity of the resulting halide. On a weight percent basis, the amount of halide will generally range from about 1 to 25, more usually from about 1 to 10.

The haloalkane and alkylene polyamine or polyalkylene polyamine may be brought together neat or in the presence of an inert solvent, particularly a hydrocarbon solvent. The inert hydrocarbon solvent may be aliphatic or aromatic. Also, aliphatic alcohols may be used by themselves or in combination with another solvent, when capable of dissolving the reactants.

The reaction may be carried out at room temperature (20° C.), but elevated temperatures are preferred. Usually, the temperature will be in the range of from about 100° to 225° C. Depending on the temperature of the reaction, the particular halogen used, the mole ratios and the particular amine, as well as the reactant concentrations, the time may vary from 1 to 24 hours, more usually from about 3 to 20 hours. Times greatly in excess of 24 hours do not particularly enhance the yield and may lead to undesirable degradation. It is therefore preferred to limit the reaction time to fewer than 24 hours.

The mole ratio of haloalkane to alkylene amine will generally be in the range from about 0.2 to 10 moles of alkylene amine per mole of haloalkane, more usually 0.5 to 5 moles of alkylene amine per mole of haloalkane. The mole ratio will depend upon the amount of halogen present in the haloalkane, the particular halogen and the desired ratio of hydrocarbon to amine. If complete suppression of polysubstitution of the alkylene polyamines is desired, then large mole excesses of the amine will be used.

Small amounts of residual halogen in the final composition are not deleterious. Generally, the residual halogen as bound halogen will be in the range of 0 to 10 weight percent of the composition. Small amounts of halogen may be present as the hydrohalide salt of the hydrocarbon substituted alkylene polyamines.

Generally, the hydrocarbons used will have aliphatic unsaturation. In particular instances, the amines may react in a way resulting in the elimination of hydrogen halide, introducing further aliphatic unsaturation into the hydrocarbon radical. Therefore, the hydrocarbon radicals usually will be olefinically unsaturated. However, the olefinic unsaturation does not significantly affect the utility of the product, and when available, saturated aliphatic halide may be used.

After the reaction has been carried out for a sufficient length of time, the reaction mixture may be extracted with a hydrocarbon medium to free the product from any low molecular weight amine salt which has formed. The product may then be isolated by evaporation of the solvent. Further separation from unreacted hydrocarbon or purification may be carried out as desired, e.g., chromatography.

Depending on the particular application of the composition of this invention, the reaction may be carried out in the medium in which it will ultimately find use and be formed at concentrations which provide a concentrate of the detergent composition. Thus, the final reaction mixture may be in a form to be used directly upon dilution in lubricating oils or fuels.

PREPARATION OF SPECIFIC COMPOSITIONS

The following examples are offered by way of illustration and not by way of limitation.

Example A

Into a reaction flask was introduced 950 g. of polyisobutylene (approximate molecular weight=950) dissolved in 1,000 ml. of carbon tetrachloride. The mixture was

stirred and chlorine was introduced at a rate of 235-250 ml. per minute, the temperature being maintained at 0° C. After the reaction mixture had taken up 51 g. of chlorine, the introduction of chlorine was terminated, the carbon tetrachloride removed in vacuo and the chlorinated polyisobutylene isolated.

Example B

Into a reaction flask was introduced 225 g. of N-bromo-succinimide, 750 g. of polyisobutylene (approximately 930 average molecular weight) and 750 ml. of carbon tetrachloride, the flask swept with nitrogen and the solution heated to 70° C. while maintaining a positive nitrogen pressure on the flask. To the solution was then added dropwise 0.5 g. of benzoyl peroxide in 50 ml. of carbon tetrachloride. At the end of the addition, the solution was cooled and the succinimide filtered off. The carbon tetrachloride was removed in vacuo. Analysis: wt. percent bromine=8.86, 8.80.

Example 1

Into a reaction flask was introduced 873 g. of bromo-polyisobutylene (polyisobutylene of approximately 930 average molecular weight brominated to 4.93 weight percent bromine) and 87 g. of tetraethylene pentamine (a mixture of compounds having the average composition of tetraethylene pentamine). The reaction was stirred for one-half hour and then heated to 185° C. for about 18 hours. At the end of this time, the mixture was allowed to cool, diluted with 3 volumes of n-hexane, and the hydrobromide salt permitted to settle. The supernatant liquid was then decanted and the remaining salt extracted with ethanol and water. After evaporation of the volatile material, the final product analyzed as follows: wt. percent nitrogen=1.1; wt. percent bromine=0.2.

Example 2

Into a reaction flask was introduced 800 g. of a chlorinated paraffinic base oil (average molecular weight approximately 570 chlorinated to approximately 6.4 weight percent) and 80 g. of tetraethylene pentamine and the mixture heated at 185° C. for 6 hours. At the end of this time, the reaction mixture was cooled and diluted with 3 volumes of n-hexane and 1 volume of ethanol followed by dilute sodium carbonate and water washes. The mixture was then heated to reflux and dilute sodium carbonate added until the cloud point was reached, the phases were separated, the organic phase diluted with one volume of ethanol, and then the mixture extracted with water. The volatile products were then pumped from the organic phase. Analysis: wt. percent N=0.53; wt. percent basic N=0.36.

Example 3

Into a reaction flask was introduced 1,780 g. of brominated polyisobutylene (polyisobutylene of approximately 930 average molecular weight brominated to 8.6 weight percent bromine) and 350 g. of a mixture of polyethylene amines having an average composition of tetraethylene pentamine and allowed to stand overnight at ambient temperatures. The mixture was then heated at 150° C. for several hours (approximately 5 to 6), cooled and diluted with several volumes of n-pentane and allowed to stand. The solution was then concentrated to about one-half its original volume, about 1 liter of ethanol and about 1 liter of 10 percent aqueous sodium carbonate added. The phases were separated and the sodium carbonate extraction repeated, followed by washing the hexane phase with water. Volatile materials were removed in vacuo by heating the organic phase to 100° C., leaving a residue of 1,369 g. Analysis: wt. percent nitrogen=2.26, 2.21; wt. percent basic nitrogen=1.09; wt. percent bromine=1.08, 0.99; molecular wt.=2,318 (determined by ThermoNAM, a differential vapor pressure technique).

Example 4

Into a reaction flask was introduced 433 g. of chlorinated polyisobutylene (polyisobutylene of approximately 950 average molecular weight chlorinated to 9.3 weight percent chlorine) and 240 g. of alkylene polyamine having an average composition of tetraethylene pentamine and 640 ml. of benzene added. The mixture was heated to reflux and the benzene distilled off. The residue was then heated at 150° C. for 4 hours. After cooling the reaction mixture and diluting with mixed hexanes, 200 ml. of ethanol was added and the organic phase extracted with 10 weight percent aqueous sodium carbonate, the phases separated and the extraction of the organic phase repeated, the phases separated again and finally the organic phase washed with water. The volatile materials were then removed in vacuo. Analysis: wt. percent nitrogen=4.66, 4.76; wt. percent chlorine=3.16; molecular wt. (ThermoNAM)=1,318.

Example 5

Into a pressure vessel was introduced 1,500 ml. of a solution of 5 parts of chlorinated polyisobutylene (approximately 1,300 molecular weight) and 2 parts of benzene (the solution analyzing to 3.66 weight percent chlorine) and 300 g. of ethylene diamine (the vessel sealed and heated at 150° C. with rocking overnight). The vessel was then allowed to cool, vented and to the reaction mixture was added an equal volume of n-hexane and a one-third volume of ethanol, the resulting mixture being heated to reflux. Approximately one-third volume of water was then added, the phases separated and the hydrocarbon phase isolated. The volatile materials were removed in vacuo (and the residue analyzed). Analysis: wt. percent nitrogen=1.82, 1.83; wt. percent basic nitrogen=1.65, 1.63.

Example 6

Into a reaction flask was introduced 3,000 g. of a 70 weight percent solution in benzene of chloropolyisobutylene (polyisobutylene of approximately 1,300 molecular weight chlorinated to 4.3 weight percent chlorine) and 210 g. of alkylene polyamine having an average composition of triethylene tetramine and the mixture heated to reflux, the benzene stripped off and the mixture further heated at 170° C. for 4 hours. At the end of this time, the mixture was allowed to cool, and then diluted with equal volumes of mixed hexanes and absolute ethanol, heated to reflux and then one-third volume of 10 weight percent aqueous sodium carbonate added. The phases were separated, and the organic phase washed with water and then the volatile materials removed in vacuo. Analysis: wt. percent nitrogen=1.44; wt. percent basic nitrogen=0.89; wt. percent chlorine=1.45; molecular weight (ThermoNAM)=2,419, 2,371.

Example 7

Following the procedure described in Example 6, 1,500 g. of a 70 weight percent solution in benzene of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to ~10 weight percent) and 155 g. of diethylene triamine were combined. Analysis: wt. percent nitrogen=1.59, 1.60; wt. percent basic nitrogen=0.96, 0.97.

Example 8

Into a reaction flask was introduced 800 g. of benzene, 846 g. of chlorinated polyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to 5.6 weight percent) and 300 g. of alkylene polyamine having an average composition of triethylene tetramine and the mixture heated to reflux and benzene gradually stripped off. The temperature was then increased to 175° C. and maintained for 3.5 hours. After allowing the mixture to cool, equal volumes of both mixed hexanes and 95 percent ethanol were added and the resulting solution sep-

arated into 2 equal portions. One of the portions was allowed to sit in a separatory funnel and the alcoholic phase permitted to separate. The hydrocarbon portion was separated from the alcoholic portion, washed with 10 weight percent aqueous sodium carbonate, followed by washing with water, and the volatile materials then removed in vacuo. Analysis: wt. percent nitrogen=3.03, 3.06; wt. percent basic nitrogen=2.26, 2.28.

Example 9

Into a reaction flask was introduced 600 g. of chloropolyisobutylene (polyisobutylene of approximately 950 molecular weight chlorinated to 5.6 weight percent), 550 ml. of benzene and 220 g. of alkylene polyamine of the average composition of triethylene tetramine and the mixture allowed to stand at ambient temperatures for 2 days. The benzene was then distilled off, and the temperature of the mixture raised to 150° C. and maintained for 4 hours. The usual extraction procedure using mixed hexanes and ethanol, followed by sodium carbonate and water washes was carried out and the volatile materials then removed in vacuo. Analysis: wt. percent nitrogen=4.10, 4.05; wt. percent basic nitrogen=3.07; wt. percent chlorine=0.57; molecular wt. (ThermoNAM)=1,510.

Example 10

Following the procedures of the previous examples, 1,500 g. of chloropolyisobutylene (polyisobutylene of approximately 2,700 molecular weight chlorinated to 6.11 weight percent chlorine) was combined with 350 g. of alkylene polyamine having an average composition of tetraethylene pentamine in one liter of benzene. Analysis: wt. percent nitrogen=1.53, 1.53.

Example 11

Following the procedures of the previous examples, 1,423 g. of chloropolyisobutylene (polyisobutylene of approximately 950 average molecular weight chlorinated to approximately 5 weight percent chlorine) was combined with 286 g. of an alkylene polyamine having an average composition of nonaethylene decamine (DowAmine 400 provided by the Dow Chemical Co.) in 1.4 liters of benzene. Analysis: wt. percent nitrogen=4.14, 4.20.

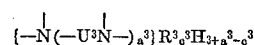
Example 12

Following the procedure of the previous examples, 600 g. of chloropolyisobutylene (polyisobutylene of approximately 2,700 average molecular weight chlorinated to about 2 weight percent chlorine) was combined with 40 g. of alkylene polyamine having an average composition of tetraethylene pentamine in 540 ml. of benzene. Analysis: wt. percent nitrogen=0.99; molecular weight (ThermoNAM)=approximately 4,400.

As already indicated, the compositions of this invention find a wide variety of uses under a wide variety of conditions. The subject compositions find use as detergents and dispersants in lubricating oils for internal combustion engines, automobile engines, in two-cycle engines, as well as in fuels for internal combustion engines, particularly gasoline engines.

UTILITY

Preferred compositions which find use in lubricating oils, both for the automobile and the diesel engines, will for the most part have the following formula:



wherein:

- U³ is alkylene of from 2 to 3 carbon atoms, preferably ethylene;
 a³ is an integer of from 1 to 5, more usually from 2 to 4;
 c³ is an integer or fractional number in the range of from 1 to 3, more usually in the range of 1 to 2, and equal to or less than the number of amine nitrogen atoms,

preferably on the average less than the number of amine nitrogen atoms; and
 R³ is a branched chain aliphatic hydrocarbon radical derived by polymerization of olefins of from 3 to 4 carbon atoms and of from about 700 to 3,000 molecular weight, more usually from about 750 to 2,800 average molecular weight. The preferred R groups are polypropylene and polyisobutylene.

The detergents may be prepared as concentrates having as high as 80 weight percent of the detergent in lubricating oil. Generally, concentrates will vary from about 10 to 80 weight percent. However, when the oil is to be used in the engine, the amount of the detergent generally will vary from about 0.1 to 15 weight percent, more usually from 0.25 to 10 weight percent. The lubricating oil compositions may therefore vary in the amount of detergent from 0.1 to 80 weight percent.

The compositions of this invention can be used with various base oils which find use as lubricating oils. Naturally occurring base oils include naphthenic base, paraffin base, asphaltic base and mixed base lubricating oils. Synthetic hydrocarbon oils include alkylene polymers, such as polymers of propylene, butylene, 1-octene, and mixtures thereof and alkylated aromatic hydrocarbons. Non-hydrocarbon lubricating oils include: alkylene oxide type polymers; carboxylic acid esters such as octyl adipate, nonyl azelate, decyl suberate, butyl alkenylsuccinate, etc.; also, inorganic esters such as phosphates and silicates.

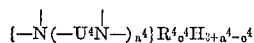
The above base oils may be used individually or in combination, whenever miscible or made so by the use of mutual solvents.

Preferably, the detergents of this invention are used in lubricating oils with an oxidation inhibitor and extreme pressure agent. The preferred inhibitors are metal dithiophosphates, particularly zinc O,O-di(hydrocarbyl) phosphorodithioate, where the hydrocarbyl groups are generally from 4 to 36 carbon atoms. (Hydrocarbyl is an organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic, aromatic or combinations thereof, e.g., aralkyl or alkaryl, and may be aliphatically saturated or unsaturated, e.g., ethylenic unsaturation.) Preferably, the hydrocarbyl groups are alkyl or alkaryl groups. Also, S-alkyl and S-polyalkyleneoxy esters of the phosphorodithioate may be used. Usually, about 6 to 50 mM./kg. of the phosphorodithioate is used in the oil.

Other additives may also be included in the lubricating oil. These additives include pour point depressants, viscosity index improvers, antiwear agents, rust inhibitors, corrosion inhibitors, other detergents and dispersants, etc. Generally, the total amount of additives exclusive of the detergent will be in the range of from about 0.1 to 5 weight percent of the lubricating oil composition.

A special situation in which the detergents of this invention are employed in lubricating oils are lubricating oils for two-cycle engines. In the two-cycle engine, the oil is incorporated with the fuel and burned directly in the piston chamber.

Preferred compositions for use in the two-cycle engine oil have the following formula:



wherein:

U⁴ is alkylene of from 2 to 3 carbon atoms, preferably ethylene;

a⁴ is an integer of from 1 to 4, preferably 2 to 4;

b⁴ is an integer or fractional number of from 1 to 2, preferably of from 1 to 1.5; and

R⁴ is a branched chain aliphatic hydrocarbon radical derived from a polyolefin obtained from olefins of from 3 to 4 carbon atoms and having a molecular weight in the range of about 650 to 3,000, more usually from about 750 to 2,000. The preferred polymers are polypropylene and polyisobutylene.

Generally, hydrocarbonaceous lubricating oils will be used, particularly petroleum derived, such as the mixed base, paraffinic and naphthenic base oils. Moreover, in place of phosphorodithioate inhibitors, other oxidative inhibitors such as bis(phenols), etc. may be used. When phosphorodithioate additives are used, concentrations in the oil may be as low as one mM./kg. Finally, a halide scavenger for the lead may also be added, usually to enhance the halide already present in the gasoline. Alkylene halide scavengers such as ethylene dibromide may be used with the detergent compositions of this invention, but aryl halides, e.g., dichlorobenzene, are preferred. Other additives, already described for the lubricating oils, may also be included.

EVALUATION

In order to demonstrate the wide applicability of the compounds within the scope of this invention, various compounds were tested under a wide variety of conditions simulating a variety of situations in which lubricating oils are used. Three different engine tests were carried out of varying severity and varying demands on detergents to demonstrate the excellent effectiveness of the compositions of this invention in lubricating oils.

The first test was the L-1 Supp. 1 (MIL-L-2104B, Supp. 1 Specifications). The oil was formulated containing 0.03 weight percent nitrogen and 8 mM./kg. of O,O-dialkyl phosphorodithioate (alkyl of from 4 to 6 carbon atoms) in a Mid-Continent SAE 30 base oil. The test was carried out for 120 hours, the following table indicating the results.

TABLE I

	Grooves ¹	Lands ²
Example:		
1.....	4-0.5-0-0	75-0-75
2.....	4-1-2-1	435-100-25
Base oil.....	³ 38-18-10-10	³ 800-800-800

¹ Measured on a rating of 0 to 100, 100 being completely filled.

² Measured on a rating of 0 to 800, 800 being completely black.

³ Tested under the less severe L-1 conditions (MIL-L-2104A).

To further demonstrate the effectiveness as detergents and dispersants of the compositions of this invention, a number of compositions were tested under Caterpillar 1-G conditions (MIL-L-45199). To a Mid-Continent SAE 30 base oil was added the detergent and zinc O,O-di(alkylphenyl) phosphorodithioate (the alkyl is polypropylene of an average of 14 carbon atoms). The test was carried out for 60 hours. The following results were obtained.

TABLE II

	Wt. percent of candidate detergent	Phosphorodithioate, mM./kg.	Grooves ¹	Lands ¹	U.H. ²
Example:					
3.....	6.76	18	24-2.3-0-0.2	135-15-40	-----
4.....	4.1	12	58-5-0.6-0.3	510-35-40	-----
5.....	4.04	12	15-2-0-0	191-7-10	7.0
6.....	5.25	12	12-3-0-0	85-0-0	7.5
7.....	4.62	12	43-4-1-1	70-0-0	7.5
8.....	2.00	8	21-5-0-0	170-50-65	7.5
9.....	3.5	12	12-2.5-0.2-0.2	125-45-25	-----
10.....	4.80	8	58-3-0-0	155-10-5	6.4
11.....	3.7	13	69-9.2-2.4-0.9	745-420-185	-----
Base oil.....		12	93-15-5-3	500-800-370	-----

¹ Used the same rating as in Table I.

² Rated 0 to 10, 10 being completely clean.

As a further test of the usefulness of the compositions of this invention in lubricating oils, a modified FL-2 test procedure, as described in June 21, 1948 report of the Coordinating Research Council, was employed. This test simulates automobile engine performance. A standard procedure requires the maintenance of a jacket temperature of 95° F. and a crankcase oil temperature of 155° F.

The Yamaha engine test uses a 75 cc. Model YG-1 motorcycle engine. The same conditions as described for the McCulloch engine are also used for the Yamaha engine.

The following table indicates the results obtained with a variety of detergents in the McCulloch engine and in the Yamaha engine tests.

TABLE IV

	Wt. percent in oil of candidate detergent		Ring sticking		G.D. No. ²		Land dep. ³		Exh. ports ⁴	Piston und. ⁵	Total rating
	PV ¹		Top	2nd	Top	2nd	Top	2nd			
McCulloch											
Example:											
5.....	7	9.2	360	F	-----	6	500	250	5	8.3	37.0
6.....	9	7.5	360	F	-----	8	700	640	7	7.8	30.8
Base oil.....		6.4	360	F	-----	5	580	610	10	6.0	28.7
Yamaha											
Example 5.....	7	8.6	360	F	-----	10	640	620	12	6.2	30.2
Base oil.....		6.0	360	160	-----		700	750	15	1.4	19.6

¹ PV—piston varnish, 0-10, 10 being clean.

² G.D. No.—groove deposit number, 0-10, 10 being clean.

³ Land dep.—land deposit number, 0-800, 800 being black.

⁴ Exh. ports—exhaust ports, 0-100% blocked.

⁵ Piston und.—piston underhead, 0-10, 10 being clean.

at 2,500 r.p.m. and 45 brake horsepower for 40 hours (closely simulating the relatively "cold" engine conditions which are normally experienced in city driving). At the end of each test, the engine is dismantled and the amount of total sludge (rating of 0 to 50, no sludge being 50) and clogging of the rings and oil screen (rating of 0 to 100, no clogging being 0) is determined. Also, the piston varnish is rated (rating of 0 to 10, no varnish being 10) and the total varnish is evaluated (rating of 0 to 50, no varnish being 50). The above test was modified by increasing the time and periodically raising the oil sump temperature from 165° F. to 205° F. and the water jacket temperature from 95° to 170° F.

Using a Mid-Continent SAE 30 base stock, each candidate detergent was employed at concentrations to provide a constant weight percent of nitrogen; also included in the oil was 10 mM./kg. of zinc O,O-di(alkyl) dithiophosphate (alkyl of from 4 to 6 carbon atoms) and 2 mM./kg. of zinc O,O-di(alkylphenyl) dithiophosphate (alkyl is polypropylene of from 12 to 15 carbon atoms). The following table indicates the results obtained.

TABLE III

Example:	Wt. percent of candidate detergent	Piston varnish	Total varnish	Total sludging	Clogging		Time, hrs.
					Ring	Screen	
4.....	0.98	3.5	16	35	27	20	80
5.....	3.50	4.3	23	48	2	4	100
6.....	2.64	4.5	14	37	25	3	100
7.....	1.44	4.1	23	41	18	10	100
8.....	4.35	4.3	17	49	0	1	100
Base oil ¹							

¹ Engine stopped in approximately 12 hours because it was unable to run any further.

The results demonstrate that the branched chain hydrocarbon substituted polyamines provide excellent versatility in providing detergency and dispersancy under broad variations in conditions and varying engine requirements.

Turning now to a consideration of the use of the detergents and dispersants of this invention in oils to be used in two-cycle spark ignition engines. Two different engines were used: a Yamaha engine which is used on motorcycles, and a McCulloch engine which is used for chain saws.

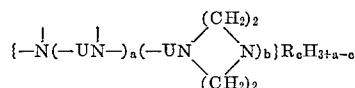
In the McCulloch engine test, the engine is a Model 1-81 approximately 85 cc. displacement. The test is carried out for 10 hours, the engine being run at 7,000 r.p.m., at a temperature of 435° F. and with a wide open throttle. Using regular gasoline, a fuel-oil mixture in the ratio of 20:1 is prepared, the oil composition being a blend of detergent in SAE 40 grade base oil, such that the finished oil contained 0.126 weight percent nitrogen.

It is evident from the foregoing results that the compositions of this invention, having a wide variety of structures and a wide variation in hydrocarbon to amine nitrogen ratio, provide effective detergency and dispersancy under a great variety of conditions. Not only are they effective in the lubricating oils of the automobile engine and in the much hotter conditions in the diesel engine, but they are also effective in two-cycle engines as well. Universality of detergency is only difficulty achieved and, of course, certain subgenera within the subject invention will operate more effectively under some conditions than they will under others. Therefore, as indicated, for particular uses narrower subgenera are preferred.

For a description of the effectiveness of the compositions of this invention as fuel detergents, reference is made to U.S. Pat. No. 3,438,757, which issued on Apr. 15, 1969.

We claim:

1. A composition of the formula:



wherein:

U is alkylene of from 2 to 6 carbon atoms;

a is an integer of from 0 to 10;

b is an integer of from 0 to 1;

a+2b is an integer of from 1 to 10;

c is an integer or fractional number in the range of 1 to 5, and equal to or less than the number of nitrogen atoms in the molecule; and

R is of from 40 to 300 carbon atoms and is an aliphatic or alicyclic branched chain hydrocarbon radical derived from petroleum hydrocarbons or polyolefins of monomers from 2 to 6 carbon atoms, with the proviso that when the monomer is ethylene, it is copolymerized with a higher homologue.

2. A composition according to claim 1, wherein:

a is of from 1 to 6;

a+2b is of from 1 to 6;

c is of from 1 to 3; and

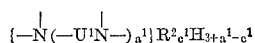
R is a polyolefin of from 50 to 200 carbon atoms.

3. A composition according to claim 1, wherein:

b is 0; and

R is a polyolefin derived from olefins of from 3 to 4 carbon atoms.

4. A composition of the formula:



wherein:

U^1 is alkylene of from 2 to 3 carbon atoms;

a^1 is an integer of from 1 to 5;

c^1 is an integer of from 1 to 5 and, on the average, equal to or less than the number of nitrogen atoms; and

R^1 is of from about 600 to 2,800 average molecular weight and is a branched chain aliphatic hydrocarbon polyolefin derived from olefins of from 2 to 6 carbon atoms, with that proviso that when the monomer is ethylene, it is copolymerized with a higher homologue.

5. A composition according to claim 4, wherein:

a^1 is of from 1 to 4;

c^1 is of from 1 to 3; and

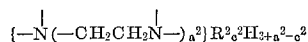
R^1 is a polyolefin derived from olefins of from 3 to 4 carbon atoms, and of about 600 to 2,800 average molecular weight.

6. A composition according to claim 5, wherein R^1 is of from about 750 to about 2,000 molecular weight.

7. A composition according to claim 4, wherein c^1 is one.

8. A composition according to claim 4, wherein c^1 is in the range of about 1.25 to 3.

9. A composition of the formula:



wherein:

a^2 is in the range of 1 to 5;

c^2 is in the range of 1 to 4 and equal to or less than the number of nitrogen atoms; and

R^2 is a branched chain aliphatic hydrocarbon group derived from olefins of from 3 to 4 carbon atoms and of an average molecular weight in the range of about 650 to 2,800.

10. A composition according to claim 9, wherein:

a^2 is in the range of 1 to 4;

c^2 is in the range of 1 to 2; and

R^2 is polypropenyl or polyisobutenyl of from about 750 to 2,000 molecular weight.

11. A polyisobutenyl ethylene diamine having from 1

to 2 polyisobutenyl groups of from about 650 to 2,800 average molecular weight.

12. A polyisobutenyl ethylene diamine having about 1 polyisobutenyl group of from about 650 to 2,800 average molecular weight.

13. A polypropenyl ethylene diamine having from 1 to 2 polypropenyl groups of from about 650 to 2,800 average molecular weight.

14. A polyisobutenyl diethylene triamine having from 1 to 2 polyisobutenyl groups of from about 650 to 2,800 average molecular weight.

15. A polypropenyl diethylene triamine having from 1 to 2 polypropenyl groups of from about 650 to 2,800 average molecular weight.

16. A polyisobutenyl triethylene tetramine having from 1 to 3 polyisobutenyl groups of from about 650 to 2,800 average molecular weight.

17. A polypropenyl triethylene tetramine having from 1 to 3 polyisobutenyl groups of from about 650 to 2,800 average molecular weight.

18. A polyisobutenyl tetraethylene pentamine having from 1 to 3 polyisobutenyl groups of from about 650 to 2,800 average molecular weight.

19. A polypropenyl tetraethylene pentamine having from 1 to 3 polyisobutenyl groups of from about 650 to 2,800 average molecular weight.

20. A lubricating oil composition having from 0.1 to 80 weight percent of a composition according to claim 1 and an oil of lubricating viscosity.

21. A lubricating oil composition having from 10 to 80 weight percent of a composition according to claim 1 and an oil of lubricating viscosity.

22. A lubricating oil composition having from 0.1 to 80 weight percent of a composition according to claim 4 and an oil of lubricating viscosity.

23. A lubricating oil composition having from 0.1 to 80 weight percent of a composition according to claim 9 and an oil of lubricating viscosity.

References Cited

UNITED STATES PATENTS

3,275,554	9/1966	Wagenaar	252—50
3,438,757	4/1969	Honnen et al.	44—72X
3,454,555	7/1969	Van der Voort et al.	252—50X
3,485,601	12/1969	Mehmedbasich	44—72X

PATRICK P. GARVIN, Primary Examiner

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44—63, 72; 260—268, 268 PI, 583 P